

**FORMATION OF “CHEMICALLY PURE” MAGNETITE FROM Mg-Fe-CARBONATES: IMPLICATIONS FOR THE EXCLUSIVELY INORGANIC ORIGIN OF MAGNETITE AND SULFIDES IN MARTIAN METEORITE ALH84001.** D. C. Golden<sup>1</sup>, D. W. Ming<sup>2</sup>, H. V. Lauer, Jr.<sup>3</sup>, R. V. Morris<sup>2</sup>, A. H. Trieman<sup>4</sup> and G. A. McKay<sup>2</sup>. <sup>1</sup>ESCG-Hamilton Sundstrand, Houston, TX; <sup>2</sup>Astromaterials Research and Exploration Science Directorate, NASA Johnson Space Center, Houston, TX ([douglas.w.ming@nasa.gov](mailto:douglas.w.ming@nasa.gov)); <sup>3</sup>ESCG-Barrios Technology, Ltd., Houston, TX; <sup>4</sup>Lunar and Planetary Institute, Houston, TX

**Introduction:** Magnetite and sulfides in the black rims of carbonate globules in Martian meteorite ALH84001 have been studied extensively because of the claim by McKay et al. [1] that they are biogenic in origin. However, exclusively inorganic (abiotic) processes are able to account for the occurrence of carbonate-sulfide-magnetite assemblages in the meteorite [2-6]. We have previously precipitated chemically zoned and sulfide-bearing carbonate globules analogous to those in ALH84001 (at  $\leq 150^\circ\text{C}$ ) from multiple fluxes of variable-composition Ca-Mg-Fe-CO<sub>2</sub>-S-H<sub>2</sub>O solutions. Brief heating of precipitated globules to  $\sim 470^\circ\text{C}$  produced magnetite and pyrrhotite within the globules by thermal decomposition of siderite and pyrite, respectively [4,5]. We have also shown that morphology of magnetite formed by inorganic thermal decomposition of Fe-rich carbonate is similar to the morphology of so-called biogenic magnetite in the carbonate globules of ALH84001 [7].

Magnetite crystals in the rims of carbonate globules in ALH84001 are chemically pure [8] [Note: “Chemically pure” is defined here as magnetite with Mg at levels comparable or lower than Mg detected by [8] in ALH84001 magnetite]. A debate continues on whether or not chemically pure magnetite can form by the thermal decomposition of mixed Mg-Fe-carbonates that have formed under abiotic conditions. Thomas-Keppta et al. [9] argue that it is not possible to form Mg-free magnetite from Mg-Fe-carbonate based on thermodynamic data. We previously suggested that chemically pure magnetite could form by the thermal decomposition of relatively pure siderite in the outer rims of the globules [5]. Mg-Fe-carbonates may also thermally decompose under conditions conducive for formation of chemically pure magnetite [3,6]. In this paper we show through laboratory experiments that chemically pure magnetite can form by an inorganic process from mixed Mg-Fe-carbonates.

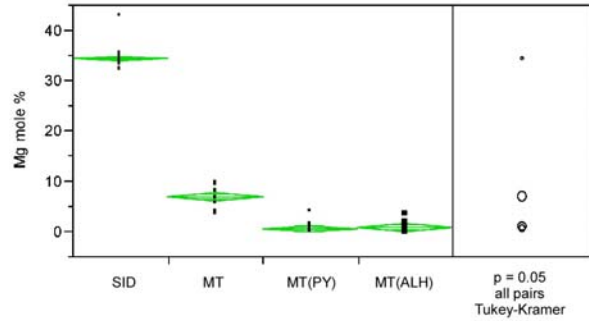
**Materials and Methods:** A natural siderite sample ( $<150\ \mu\text{m}$ , 64.3 mol % Fe, 34.5 mol % Mg and 1.2 mol % Mn) from Copper Lake, Antigonish County, Nova Scotia and a natural pyrite ( $<150\ \mu\text{m}$ , near FeS<sub>2</sub> composition with minor silicate inclusions) of unknown origin were used as the Mg-siderite and sulfide sources for experiments. Siderite (200 mg), pyrite (50 mg), and siderite + pyrite (200 mg of siderite and 50 mg of pyrite in separate containers) were heated to  $350^\circ\text{C}$  in evacuated and sealed quartz tubes (closed

system). Temperature was ramped up at  $1^\circ\text{C}/\text{min}$ . Samples were kept at set temperature ( $\sim 350^\circ\text{C}$ ) for approximately 9 days and then allowed to cool to ambient temperatures. A portion of each recovered sample was dispersed in triple distilled H<sub>2</sub>O and mounted on C-substrates attached to Cu grids for transmission electron microscope (TEM) studies. The remaining sample was treated with 20% acetic acid followed by multiple washings with distilled H<sub>2</sub>O to remove carbonates and soluble salts. The residue was dispersed in distilled H<sub>2</sub>O and mounted for TEM analysis in a similar procedure as samples washed only in distilled water.

Magnetite crystals were extracted from ALH84001 carbonate globules using the same acetic acid procedure as described above. Chemical compositions of carbonates were determined by Cameca SX100 electron microprobe and magnetite grains by energy dispersive spectroscopy (EDS) using a JEOL 2000FX TEM equipped with a Thermo Noran System Six EDS (beam  $\sim 100\ \text{nm}$ , 5000 counts).

**Results and Discussion:** Together with residual siderite and pyrite, magnetite and pyrrhotite were the reaction products of siderite plus pyrite heated at  $350^\circ\text{C}$  in a closed system. Submicron-sized, euhedral magnetite and platy pyrrhotite crystals formed on siderite surfaces and along cleavage cracks in the siderite. Magnetite and residual siderite were reaction products present in experiments where only siderite was heated at  $350^\circ\text{C}$  in a closed system. Pyrite underwent little or no change where only pyrite was heated to  $350^\circ\text{C}$  in a closed system.

The Mg compositions of the natural siderite, magnetite produced from siderite only and magnetite produced from siderite + pyrite starting materials are compared to Mg compositions of magnetite extracted from the rims of carbonate globules in ALH84001 in Fig. 1. The Copper Lake siderite has an average Mg composition of 34.5 mole %. Magnetite that formed after heating only siderite at  $350^\circ\text{C}$  in a closed system had an average Mg composition of 7.1 mole %. Chemically pure magnetite (Mg  $<1\ \text{mol } \%$ ) was produced in experiments where siderite + pyrite starting materials were heated  $350^\circ\text{C}$  in a closed system. The compositions of magnetite from ALH84001 carbonate globules and magnetite that formed from heating siderite in the presence of pyrite are indistinguishable ( $p < 0.05$ , Tukey-Kramer test).



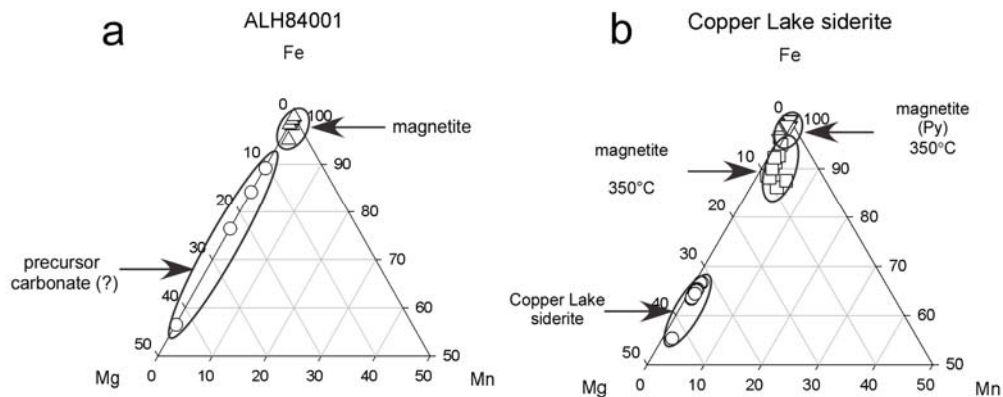
**Figure 1.** Magnesium composition of the precursor natural Mg-siderite (SID) and magnetite (MT) reaction products after heating at 350°C [siderite heated alone (MT) and with pyrite (MT(PY))], and magnetite from ALH84001 carbonates (MT(ALH)). Overlapping circles on the right for MT(PY) (Mg =  $0.5 \pm 0.5$  mol %) and MT(ALH) (Mg =  $1.0 \pm 0.9$  mol %) indicate no significant difference at  $p < 0.05$ . Top and bottom edges of green diamonds represent 95% confidence intervals.

The magnetite-containing rim region of ALH84001 carbonate globules is predominantly Fe and Mg with very low Mn [6]. Mn is not expected as an important impurity in the magnetite rims of ALH84001 carbonates because of the low Mn in the carbonate. Compositions of the thick inner magnetite rim of ALH84001 carbonates may represent the precursor carbonate composition (data from [6]), which is plotted along with the analyses of the acetic acid extracted ALH84001 magnetite crystals (our data) in Fig. 2a. The compositional plot in Fig. 2b shows the compositions of siderite and magnetite from our experimental studies. The most notable trend in these ternary plots is that magnetite is chemically pure, yet the precursor carbonate in ALH84001 and our experimental studies have high Mg. Mg may have exsolved as Mg-rich carbonate (and/or periclase) as suggested by the relatively high Mg in acetic acid

extracts. This trend indicates that chemically pure magnetite can form in ALH84001 by the thermal decomposition of Mg-Fe-carbonates. Treiman [6] and Koziol [10] suggest that chemically pure magnetite will form from Fe-Mg-carbonates at low  $f_{O_2}$  and low temperature (e.g., 350°C). Thus it appears that the  $f_{O_2}$  in our closed system experiments is sufficiently low such that Mg is excluded from the magnetite structure during thermal decomposition of the Fe-Mg-carbonate and pyrite. Chemically pure magnetite formed only in the presence of pyrite suggesting that pyrite was necessary for maintaining a sufficiently low  $f_{O_2}$  in our closed system experiments.

**Conclusions:** In the presence of pyrite, essentially Mg-free magnetite formed from thermal decomposition of Fe-Mg-carbonates similar to those in ALH84001. This magnetite is indistinguishable in composition from magnetite found in ALH84001 carbonate globules. We infer that the presence of pyrite held the  $f_{O_2}$  within the range for forming Mg-free magnetite. Formation of chemically pure magnetite from Mg-Fe-carbonates in our experimental studies suggests that chemically pure magnetite in ALH84001 can form by exclusively inorganic processes during the thermal decomposition of Mg-Fe-carbonate in the presence of pyrite under closed atmospheric conditions.

**References:** [1] McKay D.S., et al. 1996. *Science*, 273:924-930. [2] Brearley, A.J. 1998. *LPSC XXIX*, Abst. #1451. [3] Brearley, A.J. 2003. *Meteor. & Planet. Sci.*, 38:849-870. [4] Golden, D.C., et al. 2000. *Meteor. & Planet. Sci.*, 35:457-465. [5] Golden, D.C., et al. 2001. *Amer. Min.*, 86:370-375. [6] Treiman, A.H. 2003. *Astrobiol.*, 3:369-392. [7] Golden, D.C. et al. 2004. *Amer. Min.*, 89:681-695. [8] Thomas-Keperta, K.L., et al. 2000. *Geochim. Cosmochim. Acta* 64:4049-4081. [9] Thomas-Keperta, K.L., et al. 2002. *LPSC XXXIII*, Abst. # 1911. [10] Koziol, A.M. 2004. *Amer. Min.*, 89:294-300.



**Figure 2:** Compositions of (a) “precursor carbonate” and magnetite in ALH84001 and (b) Copper Lake siderite and magnetite that has formed from siderite with (magnetite(Py)) and without pyrite (magnetite) at 350°C in a closed system. The precursor carbonate in (a) is the magnetite inner rim composition of ALH84001 carbonates (data from [6]) and may represent the composition of carbonate which produced the magnetite in ALH84001.